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The screening of $4f$ moments and delocalization in the compressed light rare earths

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Spin and charge susceptibilities and the $4f^n$, $4f^{n\pm 1}$ configuration weights are calculated for compressed Ce ($n=1$), Pr ($n=2$), and Nd ($n=3$) metals using dynamical mean field theory combined with the local-density approximation. At ambient and larger volumes these trivalent rare earths are pinned at sharp $4f^n$ configurations, their $4f$ moments assume atomic-limiting values, are unscreened, and the $4f$ charge fluctuations are small indicating little f state density near the Fermi level. Under compression there is dramatic screening of the moments and an associated increase in both the $4f$ charge fluctuations and static charge susceptibility. These changes are coincident with growing weights of the $4f^{n-1}$ configurations, which it is argued are better measures of delocalization than the $4f^{n+1}$ weights which are compromised by an increase in the number of $4f$ electrons caused by rising $6s$, $6p$ bands. This process is continuous and prolonged as a function of volume, with strikingly similarity among the three rare earths, aside from the effects moderating and shifting to smaller volumes for the heavier members. The observed α - γ collapse in Ce occurs over the large-volume half of this evolution, the Pr analog at smaller volumes, and Nd has no collapse.

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I. INTRODUCTION

The trivalent rare earth series is an important but not well understood test ground for the study of strong electron correlation, and the manner in which its effects diminish as the $4f$ electrons delocalize under pressure. These metals appear initially to remain localized as they pass through a sequence of high-symmetry close packed phases keyed to $3d$ -band occupancy,¹ and then on further compression, eventually reach low-symmetry early-actinide-like structures suggestive of f -electron bonding.²⁻⁴ Transitions in the region between these two limits may exhibit unusually large volume changes. While not the case for Nd,^{5,6} the γ - α “volume collapse” of 15% in Ce is well known,⁷⁻¹⁰ and similar collapses occur in Pr (9%),¹¹⁻¹⁵ Gd (5%),¹⁶ and Dy (6%).¹⁷ Magnetic properties at atmospheric pressure are generally consistent with atomic $4f$ Hund’s rules moments,^{4,18} while the susceptibility for the collapsed α -Ce phase⁷ and for early actinide analogs¹⁹ is temperature-independent, enhanced Pauli paramagnetic, indicating absent or screened moments. On the other hand, high energy neutron scattering measurements for Ce,²⁰ and x-ray emission spectroscopy for Gd,²¹ continue to detect $4f$ moments in the collapsed phases, possibly sensing underlying “bare” moments in spite of screening effects. The $4f$ electron delocalization itself may be examined using resonant inelastic x-ray scattering determination of the probabilities of finding $f^{n\pm 1}$ configurations in a compressed rare earth of nominal f^n character.^{21,22}

There are at present two viable explanations for the Ce collapse, with possible implications for the other trivalent rare earths. One is that it is driven by a Mott Transition (MT) in the $4f$ electrons,^{23,24} while the other Kondo Volume Collapse (KVC) model points to rapid volume-dependent changes in screening of the $4f$ mo-

ments by the valence electrons.²⁵⁻²⁸ The conflict between these scenarios is exaggerated by the use of incompatible approximations. Polarized local-density approximation (LDA), LDA+U, and self-interaction corrected LDA calculations have been used to support the MT picture.²⁹⁻³⁵ While valuable, these are still *static* mean-field treatments which yield either completely itinerant (no $4f$ Hubbard structure) or completely localized (Hubbard splitting but no Fermi-level $4f$ structure) solutions, thus indicating a too abrupt picture of the collapse transitions. On the other hand, the Anderson impurity model treatments²⁵⁻²⁸ used to elucidate the KVC scenario can be faulted for omitting direct f - f hybridization and Kondo lattice effects, and one may worry whether $O(1/N)$ solutions³⁶ might favor the localized limit.

The combination (LDA+DMFT)^{37,38} of LDA input with truly correlated Dynamical Mean Field Theory (DMFT)^{39,40} solutions has offered a new perspective which has generally been supportive of the KVC scenario for Ce.⁴¹⁻⁴⁶ Such calculations for Ce also point to ongoing $4f$ delocalization in the relevant volume range, a critical driver of Mott transitions.^{42,43} To further clarify the behavior of the compressed trivalent rare earths, the present paper reports LDA+DMFT calculations of the $4f$ spin and charge susceptibilities and the $4f^n$, $4f^{n\pm 1}$ configuration weights for the first three members, Ce ($n=1$), Pr ($n=2$), and Nd ($n=3$). This work follows an earlier effort which examined the equation of state and spectra for the same materials.⁴⁴ Here we confirm that Ce, Pr, and Nd remain localized at pressures up through the face centered cubic (fcc, γ for Ce) phases as indicated by sharp $4f^n$ populations, unscreened moments with atomic-limiting values, and small charge fluctuations indicating little $4f$ state density overlapping the Fermi level. On subsequent compression there is rapid and dramatic screening of the moments and concurrent

increase in charge fluctuations and the static charge susceptibility. These changes are also coincident with rapid growth in the $4f^{n-1}$ configuration weights, which we argue offer a truer measure of delocalization than do the $4f^{n+1}$ weights which are complicated by the overall increase in the number of $4f$ electrons due to rising $6s$, $6p$ bands. These trends are continuous and prolonged as a function of compression, and strikingly similar among the three rare earths, suggesting a robust underlying progression which must first be acknowledged before tackling in general the location or absence of volume collapse transitions at various stages along the course of this evolution.

In the remainder of this paper, the susceptibility and configuration weight formalisms are first reviewed in Secs. II and III, respectively. Computational details are given in Sec. IV, results in Sec. V, and a summary in Sec. VI. The Appendix discusses the optimal disposition of diagonal, one-body f - f terms used here in the Quantum Monte Carlo solution of auxiliary impurity problem.

II. SUSCEPTIBILITY

The important local susceptibilities for real, multiband systems would appear to be associated with the total spin \mathbf{S} , orbital angular momentum \mathbf{L} , total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and charge

$$\chi_S(\tau) = \langle T_\tau \hat{\mathbf{S}}(\tau) \cdot \hat{\mathbf{S}}(0) \rangle \quad (1)$$

$$\chi_L(\tau) = \langle T_\tau \hat{\mathbf{L}}(\tau) \cdot \hat{\mathbf{L}}(0) \rangle \quad (2)$$

$$\chi_J(\tau) = \langle T_\tau \hat{\mathbf{J}}(\tau) \cdot \hat{\mathbf{J}}(0) \rangle \quad (3)$$

$$\chi_c(\tau) = \langle T_\tau [\hat{n}_l(\tau) - n_l][\hat{n}_l(0) - n_l] \rangle, \quad (4)$$

for the electrons in some l shell (e.g., $4f$) on a particular site, and with T_τ the imaginary time τ ordering operator. In the last, \hat{n}_l is the total number operator $\sum_{m,\sigma} \hat{n}_{m\sigma}$ with $m = -l, -l+1, \dots, l$, and n_l is its generally non-integral expectation. For cubic symmetry,

$$\begin{aligned} \chi_S(\tau) &= 3 \langle T_\tau \hat{S}_z(\tau) \hat{S}_z(0) \rangle \\ &= \frac{3}{4} \sum_{m,\sigma,m',\sigma'} \sigma \sigma' \langle T_\tau \hat{n}_{m\sigma}(\tau) \hat{n}_{m'\sigma'}(0) \rangle \\ &= \frac{3}{4} \langle T_\tau [\hat{n}_\uparrow(\tau) - \hat{n}_\downarrow(\tau)][\hat{n}_\uparrow(0) - \hat{n}_\downarrow(0)] \rangle \end{aligned} \quad (5)$$

where $\hat{n}_\sigma \equiv \sum_m \hat{n}_{m\sigma}$ is the total number operator for a given spin $\sigma \equiv 2m_s = \pm 1$ summed over orbitals $m \equiv m_l$. Aside from the factor of $3/4$ this is the spin susceptibility of the two-band model of Koga *et al.*,⁴⁷ or for $\tau = 0$, the same factor times the bare local moment m_z^2 of one-band Hubbard and Anderson models. Similarly $\chi_L(\tau) = 3 \langle T_\tau \hat{L}_z(\tau) \hat{L}_z(0) \rangle$ for cubic symmetry and thus

$$\chi_L(\tau) = 3 \sum_{m,\sigma,m',\sigma'} m m' \langle T_\tau \hat{n}_{m\sigma}(\tau) \hat{n}_{m'\sigma'}(0) \rangle \quad (6)$$

which is $3/4$ times the orbital susceptibility of the two-band model of Koga *et al.*,⁴⁷ taking $l = 1/2$ and $m = -1/2, 1/2$.

Spin susceptibility $\chi_J(\tau)$

In the presence of the spin-orbit interaction, it may be more useful to work in a relativistic basis $j = l \pm 1/2$ (except just $j = 1/2$ for $l = 0$), with magnetic quantum numbers $\nu = -j, -j+1, \dots, j$. Again for cubic symmetry,

$$\chi_J(\tau) = 3 \sum_{j,\nu,j',\nu'} \nu \nu' \langle T_\tau \hat{n}_{j\nu}(\tau) \hat{n}_{j'\nu'}(0) \rangle. \quad (7)$$

For DMFT calculations which include spin orbit and the Hubbard repulsion U , but omit the Hund's rule intraatomic exchange terms, a reasonable approximation to the self energy is $\Sigma_{j,\nu,j',\nu'}(i\omega) \sim \delta_{j,j'} \delta_{\nu,\nu'} \Sigma_j(i\omega)$. A consistent approximation to $\langle T_\tau \hat{n}_{j\nu}(\tau) \hat{n}_{j'\nu'}(0) \rangle$ is

$$\begin{aligned} &\langle T_\tau \hat{n}_{j\nu}(\tau) \hat{n}_{j'\nu'}(0) \rangle \\ &\sim \begin{cases} N_j(\tau)/(2j+1) & \text{if } j=j', \nu=\nu' \\ D_{jj}(\tau)/[j(2j+1)] & \text{if } j=j', \nu \neq \nu' \\ D_{jj'}(\tau)/[(2j+1)(2j'+1)] & \text{if } j \neq j', \end{cases} \end{aligned} \quad (8)$$

where

$$N_j(\tau) \equiv \sum_\nu \langle T_\tau \hat{n}_{j\nu}(\tau) \hat{n}_{j\nu}(0) \rangle \quad (9)$$

$$D_{jj}(\tau) \equiv \frac{1}{2} \sum_{\nu \neq \nu'} \langle T_\tau \hat{n}_{j\nu}(\tau) \hat{n}_{j\nu'}(0) \rangle$$

$$D_{j \neq j'}(\tau) \equiv \frac{1}{2} \sum_{\nu \nu'} \langle T_\tau [\hat{n}_{j\nu}(\tau) \hat{n}_{j'\nu'}(0) + \hat{n}_{j'\nu'}(\tau) \hat{n}_{j\nu}(0)] \rangle \quad (10)$$

with ν ranging over the $2j+1$ states of j (similarly ν' and j'). Then

$$\chi_J(\tau) = \sum_j (j+1) [j N_j(\tau) - D_{jj}(\tau)]. \quad (11)$$

Note that at $\tau = 0$, $N_j(0) = n_j$ and $D_{jj'}(0) = d_{jj'}$ where the number of electrons in the l -shell is $n_l = n_1 + n_2$ and the associated double occupation is $d_l = d_{11} + d_{12} + d_{22}$, with subscripts 1 and 2 labelling $j = l-1/2$ and $j = l+1/2$ for $l \geq 1$, respectively.

The bare or instantaneous local moments corresponding to each of Eqs. (1-3) are given by their $\tau = 0$ values, e.g.,

$$\begin{aligned} J_b(J_b+1) &= \langle \hat{\mathbf{J}}^2 \rangle = \chi_J(\tau=0) \\ &= \sum_j (j+1) [j n_j - d_{jj}]. \end{aligned} \quad (12)$$

For f electrons with integer $n_f = n$ shell populations $0 \leq n \leq 14$, one might expect in the strongly localized, atomic limit that

$$\begin{aligned} n_1 &= \min(n, 6) \\ d_{11} &= n_1(n_1-1)/2 \\ n_2 &= \max(0, n-6) \\ d_{22} &= n_2(n_2-1)/2, \end{aligned}$$

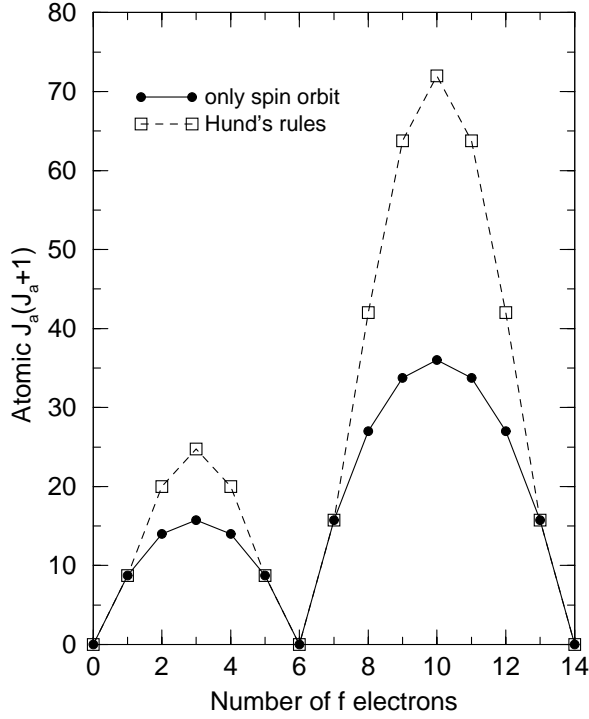


FIG. 1: Atomic moments $\langle \hat{\mathbf{J}}^2 \rangle = J_a(J_a+1)$ for the rare earths.

which leads to the filled data points (only spin orbit) in Fig. 1. Inclusion of the appropriate intraatomic exchange terms would give the correct Hund's rules values designated by the open squares. The spin-orbit-only results are seen to give the correct qualitative behavior with filling, and the correct values of $\langle \hat{\mathbf{J}}^2 \rangle$ for subshells with one or no holes or electrons. As will be seen in this paper, they also appear to give the qualitatively correct evolution from localized to itinerant behavior with compression, since much of that originates from volume-dependent changes in the double occupation which is captured correctly.

Information about *screened* moments comes from the static susceptibility $\chi_J(\omega=0)$. Given Curie-Weiss behavior, an effective moment can be extracted from the slope of $\chi_J(\omega=0)$ versus T^{-1} , thus

$$J_s(J_s+1) = T\chi_J(\omega=0) = \frac{1}{\beta} \int_0^\beta d\tau \chi_J(\tau) \quad (13)$$

At large volume and thus weak hybridization, $\hat{\mathbf{J}}$ approximately commutes with the Hamiltonian so that $\chi_J(\tau) \sim$ constant, and thus there is no screening ($J_s \sim J_b$). There is also no screening in the high temperature limit since $\chi_J(\tau) \rightarrow \chi_J(0)$ as $0 \leq \tau \leq 1/T \rightarrow 0$. At small volume (strong hybridization) and low temperature, $\chi_J(\tau)$ falls away between its maximal values at $\tau=0$ and β , leading to $J_s < J_b$. See Fig. 2.

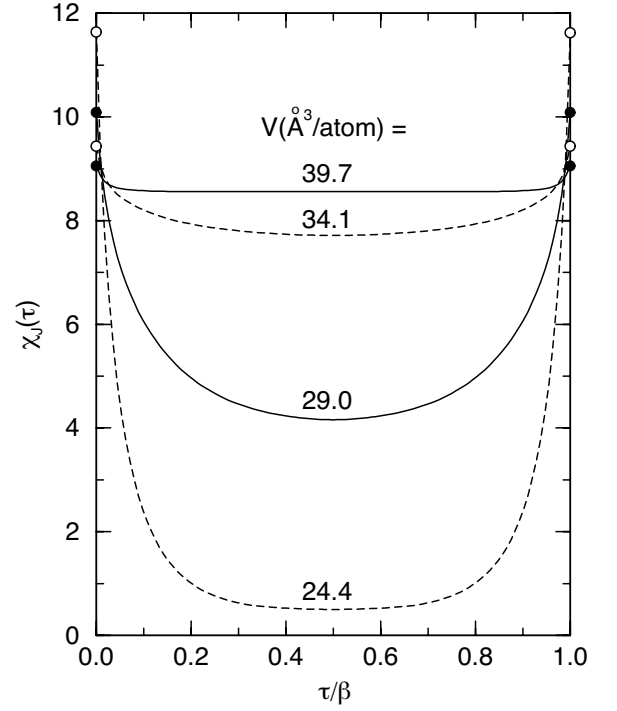


FIG. 2: $\chi_J(\tau)$ for Ce at 632 K and various volumes. The $\tau=0$ values (circles) give the bare moment squared $\langle \hat{\mathbf{J}}^2 \rangle = J_b(J_b+1)$, while the τ average gives the screened quantity $J_s(J_s+1)$. There is little screening at large volume, while the two moments are quite different at small volume. The α and γ sides of the collapse are at volumes of 27.8 and 33.1 $\text{\AA}^3/\text{atom}$, respectively, correspondingly roughly to the middle two curves. The equilibrium volume is 34.4 $\text{\AA}^3/\text{atom}$.

Charge susceptibility $\chi_c(\tau)$

The exact expression for the local charge susceptibility Eq. (4) may be written using the definitions Eqs. (9,10) as

$$\chi_c(\tau) = \sum_j N_j(\tau) + 2 \sum_{j \leq j'} D_{jj'}(\tau) - n_l^2. \quad (14)$$

Following the language of Ref. 48 the local charge “fluctuations” are

$$\begin{aligned} \langle \delta \hat{n}_l^2 \rangle &\equiv \langle (\hat{n}_l - n_l)^2 \rangle = \chi_c(\tau=0) \\ &= 2d_l - n_l(n_l - 1), \end{aligned} \quad (15)$$

while the local *static* charge “susceptibility” is

$$\chi_c^{(1)} \equiv \chi_c(\omega=0) = \int_0^\beta d\tau \chi_c(\tau). \quad (16)$$

Note that $T\chi_c^{(1)} \leq \langle \delta \hat{n}_l^2 \rangle$ since $T\chi_c^{(1)}$ is the τ average of $\chi_c(\tau)$ which drops from its $\tau=0$, β maxima of $\langle \delta \hat{n}_l^2 \rangle$ to smaller values in the mid τ range, similar to Fig. 2 for the spin case. This upper bound for $T\chi_c^{(1)}$ is of interest

since it helps to identify a large $\chi_c^{(1)}$, which signals the existence of prominent low-energy charge excitations as occurs, e.g., in the Yb valence transition.⁴⁸

Clearly $\langle \delta \hat{n}_l^2 \rangle$ and $T\chi_c^{(1)}$ are the charge susceptibility analogs of $J_b(J_b+1)$ and $J_s(J_s+1)$, respectively, for the spin case. Similarly, $\langle \delta \hat{n}_f^2 \rangle$ and $T\chi_c^{(1)}$ must approach one another in the large volume localized limit as \hat{n}_l becomes an eigenoperator of the system with vanishing hybridization. However, in contrast to the spin case, $\langle \delta \hat{n}_f^2 \rangle \rightarrow 0$ (and thus also $\chi_c^{(1)} \rightarrow 0$) in this limit for the trivalent rare earths since $n_f \rightarrow n$ and $d_f \rightarrow n(n-1)/2$, where n is the nominal integer $4f$ occupation, e.g., $n=1$ for Ce.

III. CONFIGURATION WEIGHTS

The probabilities or configuration weights w_k of finding integer k l -shell electrons on a given site are useful in discussing delocalization, and are related to $\chi_c(\tau=0) = \langle \delta \hat{n}_l^2 \rangle$ insofar as they may also be expressed as linear combinations of n_l and d_l near the localized limit. The w_k are given by

$$w_k = Z_k / \sum_{k'} Z_{k'}$$

$$Z_k = \sum_{s_k} \langle k s_k | e^{-\beta(\hat{H} - \mu \hat{N})} | k s_k \rangle. \quad (17)$$

Here \hat{H} is the Hamiltonian; \hat{N} , the total number operator for all types of electrons; μ , the chemical potential; and $\{|k s_k\rangle\}$, a complete set of eigenstates of \hat{n}_l , $\hat{n}_l |k s_k\rangle = k |k s_k\rangle$, where all other quantum numbers besides k are lumped into s_k . Evaluating the thermal expectations $\langle \dots \rangle$ of 1, \hat{n}_l , and $\hat{n}_l(\hat{n}_l-1)/2$ using the same complete basis yields

$$1 = \sum_k w_k$$

$$n_l = \sum_k k w_k$$

$$d_l = \sum_k k(k-1) w_k / 2, \quad (18)$$

which shows the statistical nature of n_l and d_l .

At sufficiently large volumes and low temperatures where only w_k for $k = n, n \pm 1$ are non-negligible, these three w_k may be expressed via Eq. (18) in terms of n_l and d_l

$$w_{n-1} = d_l - d_l^{\min}(n_l) + (|n_l - n| - n_l + n)/2$$

$$w_n = 1 - 2[d_l - d_l^{\min}(n_l)] - |n_l - n|$$

$$w_{n+1} = d_l - d_l^{\min}(n_l) + (|n_l - n| + n_l - n)/2. \quad (19)$$

Here it is convenient to use a function $d_l^{\min}(n_l)$ which is the minimum possible double occupation for an ensemble of sites whose average l -shell population is n_l . This is a

piecewise linear function which assumes the values $k(k-1)/2$ at integer k values of n_l , and may be expressed.

$$d_l^{\min}(n_l) = (n(n-1) + (2n-1)(n_l-n) + |n_l-n|)/2 \quad (20)$$

for the range $n-1 \leq n_l \leq n+1$.

Equation (19) appears intuitively to separate the effects of delocalization from those arising more simply out of changes in n_l due to a possible l -shell electron reservoir. Should n_l increase due to such a reservoir while the system is still in the strongly localized limit, where presumably $d_l = d_l^{\min}(n_l)$, then $w_{n-1} = 0$, $w_n = 1 - n_l + n$, $w_{n+1} = n_l - n$. This suggests w_{n-1} is untainted by such reservoir effects for $n_l \geq n$, or more generally from Eq. (19)

$$d_l - d_l^{\min}(n_l) = \begin{cases} w_{n+1} & n-1 \leq n_l \leq n \\ w_{n-1} & n \leq n_l \leq n+1 \end{cases}, \quad (21)$$

which we argue in Sec. V is a useful diagnostic for delocalization. By contrast the local charge fluctuations

$$\langle \delta \hat{n}_l^2 \rangle = w_{n-1} + w_{n+1} - (n_l - n)^2 \quad (22)$$

appear to mix delocalization and reservoir effects and so are therefore less useful.

IV. COMPUTATIONAL DETAILS

The LDA+DMFT calculations reported in this paper have generally been carried out as in previous work on the compressed rare earths.⁴²⁻⁴⁴ All calculations were performed for an assumed fcc structure, and at a temperature of 632 K (4 mRy). The spin-orbit interaction was included in addition to the scalar part of the $4f$ Coulomb interaction, i.e., the screened Slater integral $F^0 \equiv U_f$, however, not the higher Slater integrals (F^k , $k=2, 4, 6$) which describe the Hund's rules intraatomic exchange. While this gives the wrong values for some $4f$ moments in the localized limit, the volume-dependence accompanying delocalization of these moments may still be reasonably captured as this appears to follow from fairly general behavior in the evolution of such quantities as the double occupancy. As in the earlier papers, the LDA contribution to the present work was provided by linear muffin-tin orbital calculations in the atomic-sphere approximation as described elsewhere.⁴ The auxiliary Anderson impurity problem was solved using the Hirsch-Fye quantum Monte Carlo (QMC) algorithm,^{49,50} with results obtained for $L=80$ and 112 time slices extrapolated to $L=\infty$ assuming a $1/L^2$ dependence. This was unnecessary for $\chi_J(\tau)$ where the two L values gave essential agreement. The disposition of $U_f \hat{n}_f$ terms between the kinetic and interaction parts of the auxiliary impurity Hamiltonian in the Hirsch-Fye QMC, and the impact of this choice on Trotter corrections, is discussed in the Appendix.

The susceptibilities reported in this work were calculated within the QMC using Wick's theorem, e.g.,

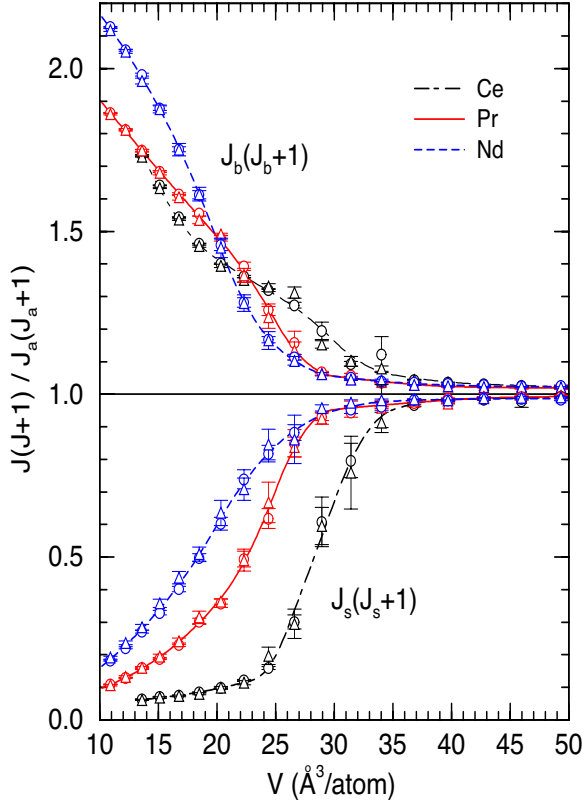


FIG. 3: (color online). Bare $J_b(J_b+1) = \chi_J(\tau=0)$ and screened $J_s(J_s+1) = T\chi_J(\omega=0)$ moments for Ce, Pr, and Nd at 632 K, relative to the atomic limiting values $J_a(J_a+1)$ of Fig. 1 for the “only spin orbit” case. Smoothed curves are drawn through the points giving $L = 80$ (circles) and 112 (triangles) results.

Eq. (154) of Ref. 40. They were obtained from runs of $\sim 350,000$ and $\sim 100,000$ sweeps for $L = 80$ and 112, respectively, using previously converged self-energies to get the input bath Green functions. Error estimates were obtained from Eq. (5.3) of Ref. 51 in conjunction with an examination of the bin-dependence of the data stored as a function of sweep.

V. RESULTS

We now present results of the susceptibility and configuration weight calculations giving first comparisons between Ce, Pr, and Nd as a function of volume, then turning to insights provided by these results in regard to the experimentally observed transitions. Definitions of the quantities calculated have been presented in Secs. II and III. The volume range studied is from 10 to 50 $\text{\AA}^3/\text{atom}$ which may be compared to 300-K experimental volumes of 14.8, 14.1, and 14.2 $\text{\AA}^3/\text{atom}$ at a pressure of 100 GPa; and 34.4, 34.5, and 34.2 $\text{\AA}^3/\text{atom}$ at 0 GPa; for Ce,^{10,52} Pr,^{13,52} and Nd,^{6,52} respectively.

Figure 3 shows results for $J(J+1)$ corresponding to

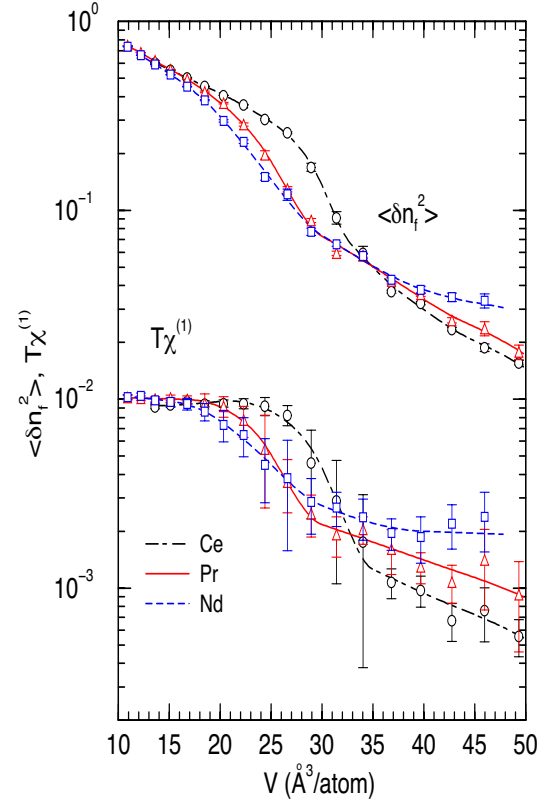


FIG. 4: (color online). Local charge fluctuations $\langle \delta \hat{n}_f^2 \rangle = \chi_c(\tau=0)$ and the static charge susceptibility $\chi_c^{(1)} = \chi_c(\omega=0)$, the latter multiplied by T , for Ce, Pr, and Nd at 632 K. Both show rapid increases under compression coincident with the changes observed in Fig. 3. $T\chi_c^{(1)}$ is everywhere more than an order of magnitude smaller than $\langle \delta \hat{n}_f^2 \rangle$ reflecting the absence of low-energy charge fluctuations, and the ratio $T\chi_c^{(1)} / \langle \delta \hat{n}_f^2 \rangle$ becomes even smaller at small volumes reflecting screening of the charge fluctuations. All points are $1/L^2$ extrapolations to $L=\infty$, with smoothed curves drawn through them.

the bare $J_b(J_b+1) = \chi_J(\tau=0)$ and screened $J_s(J_s+1) = T\chi_J(\omega=0)$ moments in Ce, Pr, and Nd, divided by the atomic limiting values $J_a(J_a+1) = 8.75, 14,$ and 15.75 , respectively, from Fig. 1. These are the “only spin orbit” values of that figure, which give the correct $J(J+1)$ for Ce, however, are 30 and 36% smaller than the true Hund’s rules values for Pr and Nd, respectively. It is particularly evident for the screened results that the changes are most abrupt and occur at the largest volumes for Ce, and then successively moderate and shift to smaller volume for Pr and then Nd, a pattern which will be seen throughout the present results. The bare moments increase with compression simply because the n_f values increase.⁵³ Since a completely random population of the $4f$ states would also have $\langle \hat{J}_z^2 \rangle$ and therefore $\langle \hat{\mathbf{J}}^2 \rangle$ increase with n_f , this does not imply the kind of coherent physical moment at the smallest volumes that one certainly has in the large volume localized limit.

Figure 4 shows the local charge fluctuations $\langle \delta \hat{n}_f^2 \rangle =$

$\chi_c(\tau=0)$ and T times the local static charge susceptibility $T\chi_c^{(1)} = T\chi_c(\omega=0)$, which are the charge analogs of the bare and screened $J(J+1)$ of Fig. 3. Both quantities show rapid increases with compression coincident with the changes seen in Fig. 3. Like the spin case these two quantities must also approach one another in the large volume limit at low temperatures, although these limiting values are not finite but 0 for the charge case. This follows from $n_f \rightarrow n$ and $d_f \rightarrow n(n-1)/2$ in this limit, where $n = 1$ (Ce), 2 (Pr), and 3 (Nd), and given that $\langle \delta \hat{n}_f^2 \rangle = 2d_f - n_f(n_f - 1)$ from Eq. (15) and $\langle \delta \hat{n}_f^2 \rangle \geq T\chi_c^{(1)}$ as discussed in Sec. II. The significance of the vanishing $4f$ charge fluctuations in the large-volume, low-temperature limit is disappearance of the Kondo resonance thus leaving a gapped $4f$ spectra overlapping the Fermi level.

Also interesting in Fig. 4 is how much smaller the local static charge susceptibility $\chi_c^{(1)}$ is compared to its limiting maximum $\langle \delta \hat{n}_f^2 \rangle / T$, e.g., $T\chi_c^{(1)} / \langle \delta \hat{n}_f^2 \rangle = 0.017, 0.031$, and 0.033 at $V = 15, 28$, and $41 \text{ \AA}^3/\text{atom}$, respectively, for Ce, with similarly small values for Pr and Nd. In contrast this ratio is $0.25, 0.58$, and 0.09 at the same volumes for the second to the last rare earth, Yb.⁴⁸ As pointed out in Ref. 48 the small ratios for Ce, Pr, and Nd constitute normal behavior where the large onsite Coulomb interaction suppresses low-energy charge excitations leading to a small local static susceptibility $\chi_c^{(1)}$. The oddball is Yb which has a valence transition from divalent (f^{14}) at large volume to trivalent (f^{13}) at small volume. The large Yb ratio 0.58 at $28 \text{ \AA}^3/\text{atom}$ is in the midst of the valence transition where the near degeneracy of f^{13} and f^{14} configurations leads to prominent low-energy charge excitations and a consequent large local static charge susceptibility. Finally, all four rare earths exhibit decreasing ratios $T\chi_c^{(1)} / \langle \delta \hat{n}_f^2 \rangle$ for compression approaching the smallest volumes considered, which reflects screening of the charge fluctuations similar to screening of the moments as has been noted.⁴⁸

The probability or configuration weight w_k of finding integer k f electrons on a given site is of some interest in understanding the manner in which the rare earths evolve from localized to itinerant character under compression. As all sites are pinned at specific integer occupations n in the large-volume, localized limit at low temperatures, then for some range of smaller volumes away from this limit only w_n and $w_{n\pm 1}$ are nonnegligible, and may be determined from the average number of $4f$ electrons n_f and their associated double occupation d_f according to Eq. (19). Figure 5 shows w_{n-1} and w_{n+1} (the latter $+0.1$ for visual clarity) calculated in this manner for Ce, Pr, and Nd ($n = 1, 2$, and 3 , respectively). Equation (19) assumes $w_n = 1 - w_{n-1} - w_{n+1}$, so that the limit $w_n = 1$, $w_{k \neq n} = 0$ is evidently being approached at large volumes.

As volume is reduced away from the localized limit, two things happen. First, for purely one-electron reasons, the $6s$ and $6p$ bands rise relative to the $4f$ levels, causing an increase in n_f ,⁵³ and thus a shift in weight from w_n to

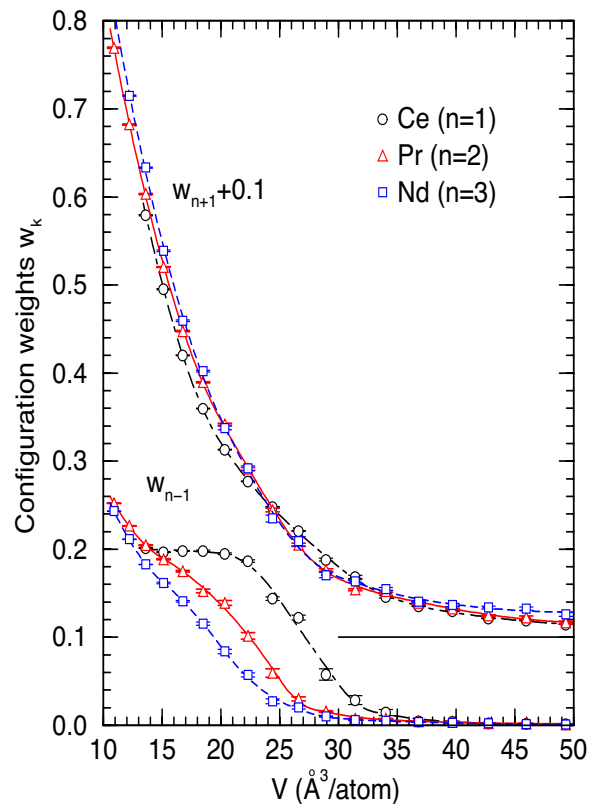


FIG. 5: (color online). Configuration weights w_{n-1} and w_{n+1} (latter $+0.1$) for Ce ($n=1$), Pr ($n=2$), and Nd ($n=3$). The former is a measure of delocalization $w_{n-1} = d_f - d_f^{\min}(n_f)$, since $n \lesssim n_f < n+1$ everywhere, and shows a dramatic rise with compression for Ce, structure which successively softens and shifts to smaller volumes in moving to Pr and then Nd. The weights w_{n+1} are complicated by the general increase in n_f with compression due to the rising $6s, 6p$ bands. All points are $1/L^2$ extrapolations to $L = \infty$, with smoothed curves drawn through them.

w_{n+1} . Second, as hybridization grows, the $4f$ electrons begin to hop to f states on neighboring sites or into and out of valence levels, causing *both* $w_{n\pm 1}$ to grow at the expense of w_n . Only w_{n-1} is a true measure of the second, delocalization effect uncomplicated by the consequences of increasing n_f .⁵⁴ Or more generally, this diagnostic for delocalization is given by Eq. (21) which is w_{n-1} for $n_f \geq n$ and w_{n+1} for $n_f \leq n$.

Figure 5 shows clear evidence of both the the rising $6s, 6p$ bands and delocalization. Note first the onset of delocalization as w_{n-1} increases with compression, and how much more abrupt this behavior is compared to the smoother w_{n+1} curves which reflect also the effects of increasing n_f . These onsets occur near the equilibrium volume of Ce ($V_0 = 34.37 \text{ \AA}^3/\text{atom}$), but at somewhat smaller volumes than the corresponding V_0 of Pr (34.54) and Nd (34.17). At the largest volumes ($V > 42 \text{ \AA}^3/\text{atom}$), w_{n+1} is an order of magnitude larger than $w_{n-1} \leq 0.003$ for all three rare earths, suggesting the behavior there is predominantly the increase in n_f

due to the rising $6s$, $6p$ bands. The Fermi level in this regime lies midway between the two Hubbard bands, and a DMFT calculation with the Hubbard I self-energy—which is incapable of generating the quasiparticle peak—has n_f pinned to 1 in the case of Ce for all volumes $V > 17.6 \text{ \AA}^3/\text{atom}$. This suggests that the large-volume shift in weight $w_n \rightarrow w_{n+1}$ is not mixed valence in the sense of the Fermi level moving into the upper Hubbard band, but rather that the rising $6s$ and $6p$ bands transfer electrons into the $4f$ quasiparticle peak, which is nonetheless still quite small in this region.

There have been experimental determinations of the Ce configuration weights $w_{0,1,2}$ using Anderson impurity model analyses of photoemission²⁷ and resonant inelastic x-ray scattering²² data, and a number of LDA+DMFT calculations^{41–44,46} of these quantities or related $n_f = 1 - w_0 + w_2$. All are consistent with $w_1 \rightarrow 1$, $w_{k \neq 1} \rightarrow 0$ in the large volume limit. There is an asymmetry between f^1 - f^0 and f^1 - f^2 mixing in solutions of the Anderson impurity model which tends to lead to the predominant transfer $w_1 \rightarrow w_0$ with growing hybridization, and thus a decrease in n_f across the γ to α collapse and $w_0 > w_2$ in the α phase.²⁸ This behavior is seen in the analyses of both experimental papers.^{22,27} The present and our earlier work^{42–44} concur with the predominant transfer $w_1 \rightarrow w_0$ across the collapse, however, has everywhere a larger w_2 than these analyses, quite possibly reflecting the impact on n_f of the rising $6s$, $6p$ bands which may not be well treated in the impurity model simulations. Thus we see a non-monotonic dip in n_f across the collapse, but generally $n_f > 1$ and $w_0 < w_2$.⁵³

We turn now to possible insights provided by the present results into the experimentally observed volume collapse transitions (shaded regions) and phase structure (demarcated by vertical solid lines) as shown in Fig. 6 for Ce,^{8–10} Pr,^{12–15} and Nd.^{5,6} At large volume only the face centered cubic (fcc) phase is labelled, which is the end of the localized, trivalent rare earth series,¹ with all three rare earths found in the preceeding, double-hexagonal close packed phase at ambient conditions. The two most dramatic theoretical diagnostics are shown for comparison, $J_s(J_s+1)$ and w_{n-1} , and while they were calculated everywhere assuming an fcc structure, it is hoped nonetheless that their volume dependence is sufficiently insensitive to structure so as to still provide useful insights. This is not an issue for Ce where both α and γ phases bounding the volume collapse are fcc.

LDA+DMFT calculations^{41–46} have consistently supported the KVC scenario^{25–28} for Ce. They show, e.g., a rapid build up of the Kondo resonance for volume reduced across the γ - α two-phase region, which is taken as a signature of the onset of screening. The present results now directly report the screened moment, and indeed one sees a 60% reduction in $J_s(J_s+1)$ from the γ to the α side of the collapse. Moreover, if the Kondo temperature T_K is defined by the condition $T\chi_J(\omega=0)/\chi_J(\tau=0) = 0.5$, then $T_K = 632 \text{ K}$ at the volume $V = 29.0 \text{ \AA}^3/\text{atom}$ (vertical dashed line) for the isothermal results in Fig. 6(a).

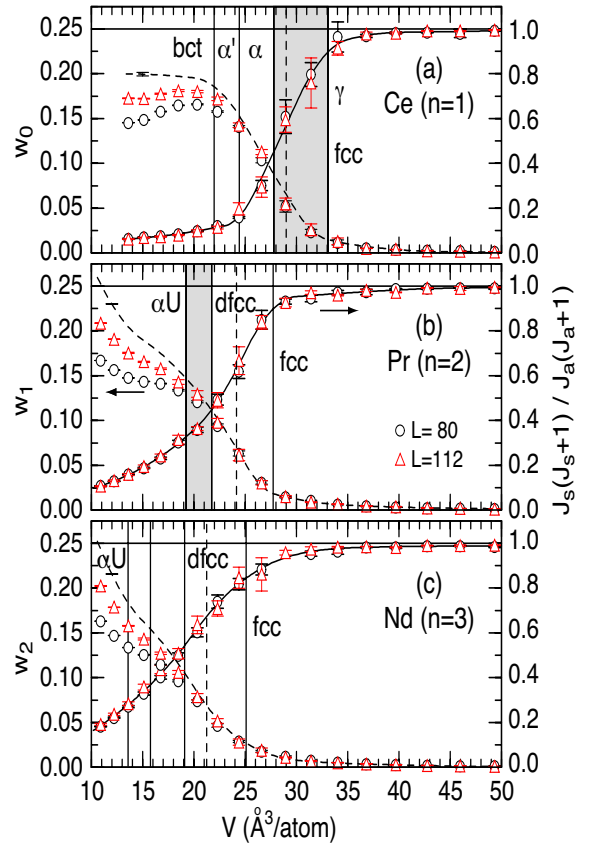


FIG. 6: (color online). Screened $J_s(J_s+1) = T\chi_J(\omega=0)$ moments (solid curves) and configuration weights w_{n-1} (dashed curves) for (a) Ce, (b) Pr, and (c) Nd at 632 K. The former are divided by the atomic limiting values $J_a(J_a+1)$ of Fig. 1 for the “only spin orbit” case. The smoothed curves are drawn through the combined $L = 80$ (circles) and 112 (triangles) points for the moments, and extrapolated to $L \rightarrow \infty$ for the w_{n-1} . All calculations were for an assumed fcc structure, however, the results are compared to the observed phases demarcated by the vertical lines, with shading for Ce and Pr indicating significant two phase regions. The vertical dashed lines show the volumes where the Kondo temperature is 632 K.

This value is consistent with the combined experimental results of Refs. 22 and 27, except for the middle 10-kbar point of the former which appears out of place given the roughly exponential behavior expected for $T_K(V)$.²⁵

The competing MT scenario for the Ce volume collapse relies on $4f$ electron delocalization as the underlying driving mechanism.^{23,24} If Eq. (21) is accepted as one suitable diagnostic, then w_0 in Fig. 6(a) suggests that the collapse also coincides with delocalization, a point that has been made previously.^{42,43} To be careful, note that Eq. (19) for the w_k does break down when configurations f^k for $|k-n| \geq 2$ become important as the itinerant limit is approached. It would seem from the present and earlier LDA+DMFT calculations that the following are all different facets of the same continuous and extended evolution with compression of a nominally f^n trivalent rare

earth: (1) transfer of $4f$ spectral weight from Hubbard side bands to a Fermi-level structure, (2) screening of the $4f$ moments, (3) growth of $4f$ charge fluctuations, and (4) dispersal of configuration weight away from $w_n=1$ to neighboring and then more distant configurations. Some of these facets look more Kondo like, and some seem more consistent with intuitive ideas of delocalization.

There is striking similarity between the theoretical diagnostics for Ce and those for Pr and Nd in Fig. 6, although the screening and delocalization effects shift to smaller volume and become more gradual for Pr, and then more so for Nd. While the Ce evolution seems to have saturated under compression on reaching the body centered tetragonal (bct) phase at about $V=22 \text{ \AA}^3/\text{atom}$ ($P=13 \text{ GPa}$),⁸ Nd has yet to reach this stage even by the smallest volume considered $10 \text{ \AA}^3/\text{atom}$ ($P\sim 365 \text{ GPa}$),⁵⁵ and Pr is intermediate. The stability fields of the distorted fcc (dfcc) structures in both Pr and Nd appear analogous to the α - γ two phase region in Ce, according to progression of the two theoretical diagnostics. Only on further compression is there a volume collapse in Pr from dfcc to α -U, while Nd passes through two additional phases before reaching the same α -U structure, absent any large volume changes. It is conceivable that this progression in collapse size and location follows simply from the shift to smaller volumes and moderation in the correlation contributions which must then compete with the ever bigger underlying benign part of the equation of state. While there are suggestions of a Van der Waals loop in the LDA+DMFT free energy corresponding to the isostructural fcc Ce collapse,^{42-44,46} one must worry about the need to include the proper Hund's rules exchange for multi- f electron Pr and Nd, as well as performing the calculations for all of the observed structures, e.g. α -U. Moreover, the Ce collapse has a critical temperature of only 480 K,⁵⁶ while for Pr, the dfcc phase is absent above about 700 K with yet a new Pr-VI phase intermediate between the α -U and fcc phases.¹⁴ These temperature sensitivities are also a reminder of the need to include lattice vibrational contributions, which may themselves further modify the nature of the collapse transitions.^{56,57}

VI. SUMMARY

We have reported LDA+DMFT calculations as a function of volume at 632 K, for the $4f$ spin and charge susceptibilities, and the probabilities of finding $4f^{n\pm 1}$ configurations in the nominally $4f^n$ trivalent rare earths Ce ($n=1$), Pr ($n=2$), and Nd ($n=3$). We find these metals to remain localized at pressures up through the fcc (γ -Ce) phases, the last structure of the initial close-packed series,¹ as indicated by sharp $4f^n$ populations, unscreened moments with atomic-limiting values, and small charge fluctuations indicating little $4f$ state density overlapping the Fermi level. On subsequent compression there is rapid and dramatic screening of the moments

and concurrent increase in charge fluctuations and the static charge susceptibility. These changes are also coincident with rapid growth in the $4f^{n-1}$ configuration weights, which we argue offer a truer measure of delocalization than do the $4f^{n+1}$ weights which are complicated by the overall increase in the number of $4f$ electrons due to the rising $6s$, $6p$ bands. Combined with earlier LDA+DMFT results, this work suggests a continuous and extended evolution with compression of a nominally $4f^n$ trivalent rare earth in which there is (1) transfer of $4f$ spectral weight from Hubbard side bands to the vicinity of the Fermi level, (2) screening of the $4f$ moments, (3) growth of $4f$ charge fluctuations, and (4) dispersal of configuration weight away from $4f^n$ to adjacent and then more distant configurations $4f^k$. The static charge susceptibility $\chi_c^{(1)}$ mirrors the volume dependence of the charge fluctuations $\langle \delta \hat{n}_f^2 \rangle$, and further indicates screening of these fluctuations at small volume, and suppression of low-energy charge fluctuations by the Coulomb interaction at all volumes.⁴⁸

The composite evolution in Ce persists until the bct phase ($V < 12 \text{ \AA}^3/\text{atom}$, $P > 13 \text{ GPa}$),⁸ whereas the α - γ two-phase region coincides with only the large-volume half or so of this progression. These effects shift to smaller volume, become more gradual, and extend over a broader volume range for Pr, and even more so for Nd, which has yet to saturate by $10 \text{ \AA}^3/\text{atom}$ ($P \sim 365 \text{ GPa}$).⁵⁵ The observed stability fields of the dfcc phases in Pr and Nd also coincide with the large-volume half of the evolution in these materials, and thus correspond to the α - γ two-phase region in Ce. The collapse is observed in Pr only on further compression, and absent in Nd. Since LDA+DMFT calculations do hint at a Van der Waals loop in the Ce free energy at about the right place,^{42-44,46} the full story for Pr and Nd may await inclusion of the Hund's rules exchange for these multi- f electron cases, assumption of the correct structures for all phases (e.g., α -U), and possibly also adding lattice vibrational contributions.^{56,57} Even so, this work suggests that the collapse transitions may not be the predominant story in the compressed trivalent rare earths, but rather consequences of an underlying and more robust evolution associated with $4f$ -electron delocalization.

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APPENDIX: TROTTER CORRECTIONS AND THE BATH GREEN FUNCTION

One issue related to application of Hirsch-Fye⁴⁹ QMC to the rare earth series deserves attention. To prepare for the Hubbard-Stratonovich transformation, one rewrites the interaction part \hat{I} of the auxiliary impurity Hamiltonian

$$U_f \sum_{\alpha < \alpha'} \hat{n}_\alpha \hat{n}_{\alpha'} = U_f \sum_{\alpha < \alpha'} [\hat{n}_\alpha \hat{n}_{\alpha'} - \frac{1}{2}(\hat{n}_\alpha + \hat{n}_{\alpha'})] + \frac{13}{2} U_f \hat{n}_f, \quad (23)$$

where α labels the 14 f states. A strict generalization of the Hirsch-Fye treatment would be to remove the $U_f \hat{n}_f$ term from the right side of in Eq. (23) and add it to the one-body or kinetic energy part \hat{K} of the Hamiltonian, with the consequent changes in unperturbed or bath Green function $\mathcal{G}(\tau)$ and also the Trotter breakup. However, for $U_f = 6$ eV and $T = 600$ K, this would lead to an f bath Green function, absent hybridization and spin orbit for simplicity, of

$$\begin{aligned} \mathcal{G}_f(\tau) &= -\frac{1}{14} \sum_{\alpha} \text{Tr}[\hat{\rho} f_{\alpha}(\tau) f_{\alpha}^{\dagger}(0)] / \text{Tr}[\hat{\rho}] \\ &\sim \frac{-e^{-\tau(\varepsilon_f + 6.5 U_f - \mu)}}{e^{-\beta(\varepsilon_f + 6.5 U_f - \mu)} + 1} \sim -10^{-300\tau/\beta}. \end{aligned} \quad (24)$$

Here $\hat{\rho} = \exp[-\beta(\hat{K} - \mu \hat{N})]$, μ is the chemical potential, \hat{N} the total electron number operator, $0 < \tau < \beta$, and we take a Ce like site energy $\varepsilon_f - \mu \sim -U_f/2$. Such a function may get into a region of underflow errors at large τ in numerical computation. Note this problem arises here in the seven-band case only because the $U_f \hat{n}_f$ term in question is 13 times larger than in the familiar one-band case. For this reason we left the $U_f \hat{n}_f$ term alone in previous work on the early rare earths,⁴²⁻⁴⁴ and took the kinetic and interaction parts of the auxiliary impurity Hamiltonian to be

$$\hat{K} = \varepsilon_f \hat{n}_f + \sum_{\lambda, \lambda'} c_{\lambda}^{\dagger} \Delta t_{\lambda \lambda'} c_{\lambda'} \quad (25)$$

$$\hat{I} = U_f \sum_{\alpha < \alpha'} [\hat{n}_{\alpha} \hat{n}_{\alpha'} - \frac{1}{2}(\hat{n}_{\alpha} + \hat{n}_{\alpha'})] + \frac{13}{2} U_f \hat{n}_f, \quad (26)$$

where λ ranges over both f and the additional bath degrees of freedom, and Δt covers the rest of the one-body terms. Keeping the $U_f \hat{n}_f$ term in \hat{I} can be handled with a minor modification of the Hirsch-Fye technique.

Since $\varepsilon_f - \mu$ itself varies from about $-0.5 U_f$ for Ce to about $-6.5 U_f$ for Lu, the choice Eq. (25) then leads to similar problems for the bath Green function of the late rare earths. A more consistent treatment for the series as a whole would be to use one of the Hubbard bands as the effective f site energy in the bath Green function, and we use the approximate position of the lower Hubbard band, $\varepsilon_{\text{LH}} = \varepsilon_f + (n-1)U_f$, with the integer n being the nominal

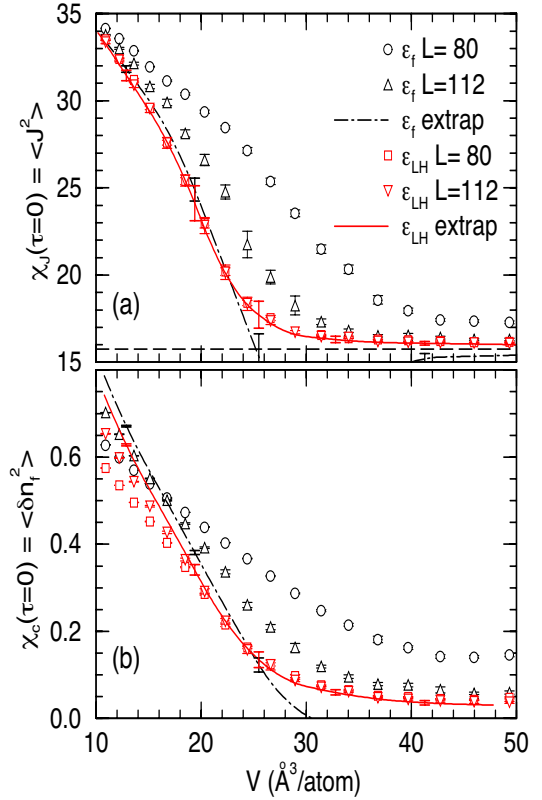


FIG. 7: (color online). Trotter corrections in (a) $\chi_J(\tau=0) = \langle \hat{J}^2 \rangle$ and (b) $\chi_c(\tau=0) = \langle \delta \hat{n}_f^2 \rangle$ for Nd as a function of volume. Results for $L = 80$ and 112 time slices are shown, using the ε_f (circles, up triangles) and ε_{LH} (squares, down triangles) effective f site energies in the QMC. The lines show L^{-2} extrapolation to $L=\infty$. It is evident that the Trotter corrections are considerably smaller using the ε_{LH} choice Eqs. (27,28). The horizontal dashed line in (a) is the atomic limiting value.

f occupation. Thus we take

$$\hat{K} = [\varepsilon_f + (n-1)U_f] \hat{n}_f + \sum_{\lambda, \lambda'} c_{\lambda}^{\dagger} \Delta t_{\lambda \lambda'} c_{\lambda'} \quad (27)$$

$$\begin{aligned} \hat{I} &= U_f \sum_{\alpha < \alpha'} [\hat{n}_{\alpha} \hat{n}_{\alpha'} - \frac{1}{2}(\hat{n}_{\alpha} + \hat{n}_{\alpha'})] \\ &\quad + (\frac{15}{2} - n) U_f \hat{n}_f, \end{aligned} \quad (28)$$

which was successfully used in Hirsch-Fye calculations for the second to last rare earth, Yb ($n=13$),⁴⁸ while for Ce ($n=1$), Eqs. (27,28) are identical to Eqs. (25,26).

We note here that even for the light rare earths such as Pr ($n=2$) and Nd ($n=3$) that Eqs. (27,28) serve to diminish the Trotter corrections relative to Eqs. (25,26). This is seen for Nd in Fig. 7, where the instantaneous spin $\chi_J(\tau=0) = J_b(J_b+1)$ and charge $\chi_c(\tau=0) = \langle \delta \hat{n}_f^2 \rangle$ susceptibilities are shown as functions of volume. Results using ε_f [Eqs. (25,26), open symbols] and ε_{LH} [Eqs. (27,28), closed symbols] as effective f site energies are given for $L = 80$ and 112 time slices. The former points are quite different indicating significant Trotter corrections, while

the latter are essentially on top of one another except for the charge case at the smallest volumes. It is reassuring that L^{-2} extrapolations to $L = \infty$ (lines) for the ε_f and ε_{LH} cases are fairly close at smaller volumes. On the other hand, extrapolation of the ε_f results yields an unphysical negative $\chi_c(\tau = 0)$ at large volumes (not

shown) indicating non L^{-2} behavior and the need for larger L . By contrast the ε_{LH} results are already converged by $L=80$ for both spin and charge cases at large volume. It is clear that Eqs. (27,28) represent the superior approach, and all results in the present paper have been obtained in this manner.

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